Exp. 2: The 1-2-3 Superconductor $YBa_2Cu_3O_7$ (Text #1)

Last week:

- Performed high-temperature, solid-state reaction to prepare $YBa_2Cu_3O_x$

Thursday:

- Determine product stoichiometry ("x")
  - *based on lost mass after heating*
  - from an iodometric titration
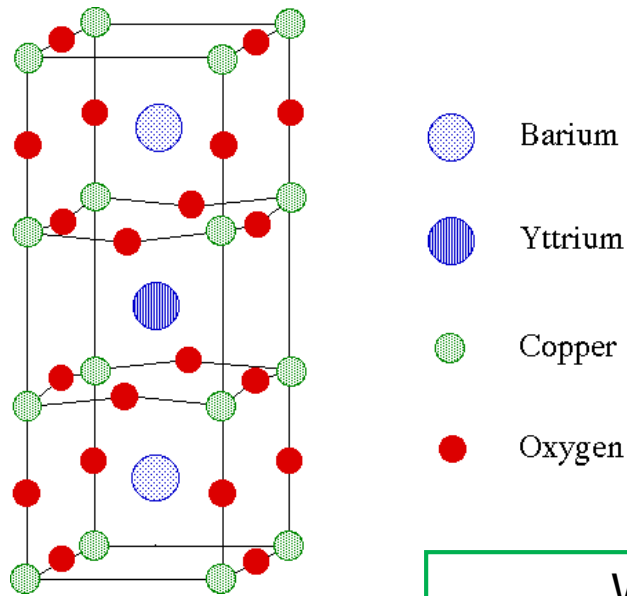- Test your product for superconductivity

Stoichiometry of $YBa_2Cu_3O_x$: Determining x

$\frac{1}{2} Y_2O_{3\,(s)} + 2\,BaCO_{3\,(s)} + 3\,CuO_{(s)} \rightarrow YBa_2Cu_3O_{x\,(s)} + 2\,CO_{2\,(g)}$

What value of 'x' is expected from stoichiometry? 6.5

Desired for superconductivity?   7

Unit cells of $YBa_2Cu_3\,O_x$ and $CaTiO_3$

Barium

Yttrium

Copper

Oxygen

What would $CaTiO_3$ (Perovskite) look like?

http://imr.chem.binghamton.edu/labs/super/superc.html

Determining *x*: From Lost Mass

$$\tfrac{1}{2}\, Y_2O_{3\,(s)} + 2\, BaCO_{3\,(s)} + 3\, CuO_{(s)} \rightarrow YBa_2Cu_3O_{x\,(s)} + 2\, CO_{2\,(g)}$$

Mass before heating – Mass after heating = ??   Mass of CO_2 lost

How can you use the lost mass of CO_2 to determine *x*?

- *Find moles of O present in lost CO_2.*

- *Use your masses of reactants to find moles of O in each; then determine moles of O in your product.*

- *Set up a proportion to relate moles of O to equivalents of O*

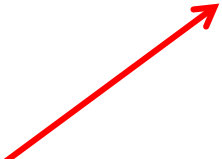What are some potential sources of inaccuracy in this method for determining *x*?

Determining *x*: From Iodometric Titration

Superconductor $YBa_2Cu_3O_7$: Expected average Cu oxidation state?

$$Y = 3^+$$
$$Ba = 2(2^+) = 4^+$$
$$O = 7(2^-) = 14^-$$
$$\overline{}$$
$$7^-$$

$$Cu = 3(x) = 7^+$$

$$x = 2.33$$

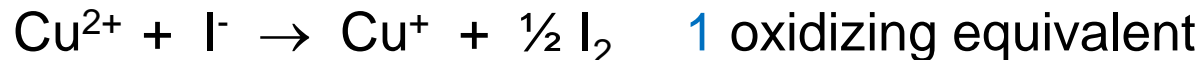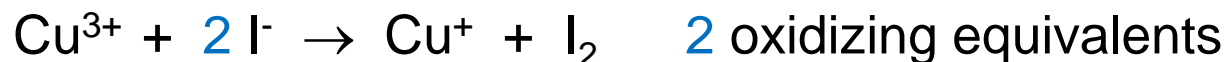What does this mean, practically?

Formally, there are two are Cu(II) ions for every one Cu(III).

(Cu(III) represents Cu centers with missing electrons in Cu-O bonds.)

In your compounds, we don't know *x*. We will determine the average oxidation state of Cu by titration and use it to find *x*.
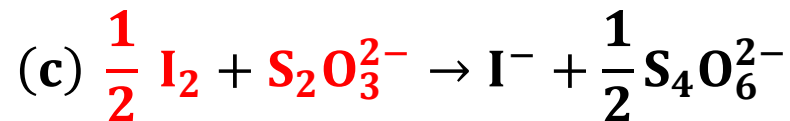
Iodometric Titrations

- Cu(II) and Cu(III) both oxidize iodide, I^-, to molecular iodine, I_2.

   $Cu^{3+} + 2\,I^- \rightarrow Cu^+ + I_2$ 2 oxidizing equivalents

   $Cu^{2+} + I^- \rightarrow Cu^+ + \frac{1}{2}\,I_2$ 1 oxidizing equivalent

- In your final titration (the one using your $YBa_2Cu_3O_x$ product, referred to as reaction a.), you will determine the amount of I_2 formed in these reactions and use it to find the total # of oxidizing equivalents, the average Cu oxidation state, and *x*.

Standardization of $S_2O_3^{2-}$ Solution

- Thiosulfate will be used for determination of the yield of I_2 following the reaction of your superconductor with I^- (reaction a).
  - It is sensitive to its environment, so its concentration must be precisely determined via standardization.

- A standard solution of IO_3^- will be used to generate an exact amount of I_2 in the presence of excess I^- (reaction b.), which is then titrated with your thiosulfate solution (reaction c).

$$\text{(b)}\ 5\,I^- + IO_3^- +\ 6\,H^+ \rightarrow 3\,I_2 + 3\,H_2O$$

$$\text{(c)}\ \frac{1}{2}\,I_2 + S_2O_3^{2-} \rightarrow I^- + \frac{1}{2}\,S_4O_6^{2-}$$

- Reaction c. will be used to determine the moles of I_2 generated from the reduction of copper, which will allow the calculation of x.

Standardization of $S_2O_3^{2-}$ Solution

- To aid in the determination of the endpoint of reaction c., a starch indicator will be added to detect the presence of **triiodide**.

- Triiodide forms when both I^- and I_2 are present in solution

$$I^- + I_2 \leftrightarrow I_3^-$$

- Towards the end of the titration, starch will be added as a triiodide indicator. Starch and triiodide react to form an intensely blue-colored complex.

- When all of the iodine is consumed, the solution will appear colorless and the endpoint is reached.

Determination of x

- You will add a pre-determined amount of your superconductor into a 10% KI solution.
  - After degassing and acidifying the solution, the solution will turn brown as the copper reacts to generate I_2, as described by reaction a., which is converted to I_3^-.

- The brown solution is then titrated to the endpoint using your standardized thiosulfate solution, as described by reaction c. The formation of a white, turbid mixture indicates reduction of all iodine to iodide.

Determination of x

1. Use your titrant volume of $Na_2S_2O_3$ to find the **total moles of I^-** present in your "superconductor" sample.

2. Approximate the **number of moles of Cu in your sample** using the mass of $YBa_2Cu_3O_x$ reacted and an approximate molecular weight for the compound, assuming x = 7.

3. Find the number of **oxidizing equivalents per mole of Cu** (i.e., ratio of moles of iodide to Cu), and use this value to determine the average oxidation state of copper in your sample:

Avg Cu ox. state = (# ox. equiv. per mole Cu) + 1

4. Use oxidation states (including your average for copper) to calculate x; report to 2 significant figures.

"Report" Due Thurs., 2/12

You will **not** write a formal lab report for this experiment. Instead, please answer each of the following questions:

1. Briefly characterize the appearance of your $YBa_2Cu_3O_x$ product and describe the results of your Meissner test for superconductivity.

2. Calculate 'x' in $YBa_2Cu_3O_x$ using each of the two methods below, showing all your calculations:
   a) Lost mass after heating
   b) Iodometric titration

3. Briefly discuss the results described in your answers to Questions 1 and 2. Which value of 'x' is more reliable and why? Did your compound display superconductivity? Are its appearance and stoichiometry consistent with the results of the Meissner test?

4. You assumed x=7 to calculate the moles of your superconductor. How much impact does this have on the subsequent steps in the calculation?

Procedural Tips

1. Remember to use the same balance to determine the "post-heating" mass of your crucible and product.

2. Weigh out the ~0.11 g of $YBa_2Cu_3O_x$ to be used in titration 3 first (record exact mass). The remainder of your product may be used for superconductivity testing.

3. All solutions have been prepared for you. Note the molar concentration or normality provided on each bottle.

4. Take your time with titrations. You will look for disappearance of blue color. Swirl the flask and wait between drops of titrant.

   a) Don't add as much titrant initially (prior to adding indicator) as is suggested in the text. Instead of adding 10 mL of $S_2O_3^{2-}$, try 7-8 mL, instead (so as not to overshoot the endpoint).